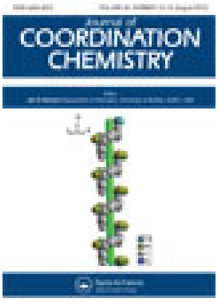

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A tetragonal molecular cage and polymeric macrocyclic complex based on a clip-like bis-pyridyl-bis-amide ligand

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A tetragonal molecular cage and polymeric macrocyclic complex based on a clip-like bis-pyridyl-bis-amide ligand

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Reactions of a bis-pyridyl-bis-amide ligand, *N*,*N*′-bis(pyridin-3-yl)-2,6-pyridinedicarboxamide (bppdca) with nickel(II) and cobalt(II) salts resulted in a tetragonal molecular cage, $[Ni_2(bppdca)_4(SCN)_4]$ (**1**), and a 1-D polymeric macrocyclic complex, $[Co(bppdca)(SO_4)(CH_3OH)(DMF)]_n \cdot nCH_3OH$ (**2**) (DMF = *N*,*N*′-dimethylformamide). Compound **1** features a tetragonal cage-like structure. In each cage, four bppdca ligands are twisted in the same direction, which endow the cage with chirality. However, because the twist or screw directions of adjacent cages are contrary, **1** is a mesomer and exhibits no chirality on the whole. Compound **2** possesses a 1-D, double-chain structure containing $Co_4(SO_4)_4(bppdca)_2$ macrocyclic subunits.

Keywords: Cage; Helicate; Metalated macrocycle; Crystal structure; Coordination polymer

1. Introduction

Synthesis of metalated macrocyclic and cage-like molecules has received attention for its structural diversity and rich physical and chemical properties [1]. To construct these supramolecular complexes, selection of appropriate organic linkers with given shape and function is a crucial step. Clip-like ligands, which are ditopic linkers possessing one coordinating arm on each side of the organic space, are good candidates for self-assembly of molecular macrocycles and cages together with transition metal ions in different coordination configurations [2]. When assembled with linearly coordinating metal ions, two clips can connect two metal nodes to form a rectangular macrocycle [3]. Further, if the metal ions are triangularly coordinated, three clips together with two metal ions can form a trigonal prism [4]. Finally, four clips together with two square-planar metal ions, such as Pd(II), can fabricate a tetragonal prism [5].

The ditopic bis-pyridyl-bis-amide ligand has flexible configurations owing to free rotation of the $N_{amide}–O_{pyridyl}$ bonds, creating structural diversity upon assembling with transition metals. Additionally, accessible hydrogen-bonding sites at amides can strengthen the stability of the obtained structures. Recently, we reported two 1-D chain-like complexes based on *N*,*N*′-bis(pyridin-4-yl)-2,6-pyridinedicarboxamide, which

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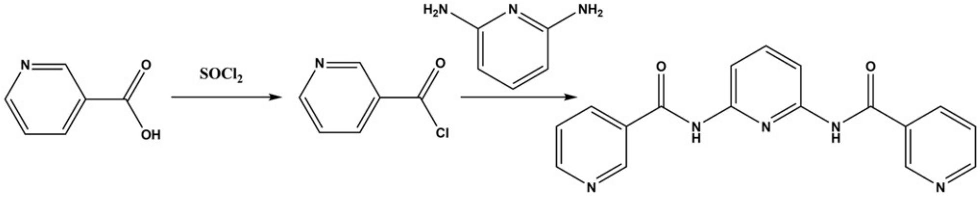

Scheme 1. Schematic representation of the synthesis of bppdca.

assemble into 3-D supermolecules through hydrogen bonding [6]. As further work, we wish to report a discrete tetragonal molecular cage with interesting chiral void and a polymeric macrocyclic complex containing $Co_4(SO_4)_4(bppdca)_2$ subunits based on a conformationally flexible clip-like ligand *N*,*N′*-bis(pyridin-3-yl)-2,6-pyridinedicarboxamide (bppdca).

2. Experimental

2.1. *General information and materials*

All reagents were of analytical grade and used as obtained from commercial sources. The ligand was synthesized according to a reported method [6].

2.2. *Syntheses*

2.2.1. Synthesis of $[Ni_2(bppdca)_4(SCN)_4]$ (1). A solution of 63.8 mg (0.2 mmol) bppdca in 5 mL DMF was added slowly to a solution of 53 mg (0.2 mmol) $NiSO_4 \cdot 6H_2O$ in 10 mL methanol at room temperature. A 19.4 mg (0.2 mmol) sample of KSCN in 10 mL methanol was then added to the clear pale green solution and stirred for 30 min. Finally, the mixture was filtered and the filtrate was allowed to stand undisturbed at room temperature. Blue crystals suitable for single-crystal X-ray diffraction were obtained after 3 weeks. The crystals were filtered, washed with methanol thrice, and dried in air (yield 38% based on bppdca). Infrared (IR) (KBr, $\nu\,cm^{-1}$): 3425(m), 2084(vs), 1655(s), 1591(s), 1526(s), 1448(s), 1309(s), 1241(s), 1128(s), 801(m), 702(m) (scheme 1).

2.2.2. Synthesis of $[Co(bppdca)(SO_4)(CH_3OH)(DMF)]_n \cdot nCH_3OH$ (2). A solution of 31.9 mg (0.1 mmol) bppdca in 5 mL DMF was added slowly to a solution of 28 mg (0.1 mmol) $CoSO_4 \cdot 7H_2O$ in 5 mL methanol at room temperature. A 9.7 mg (0.1 mmol) sample of KSCN in 5 mL methanol was then added to the clear purple solution and stirred for 30 min. Finally, the mixture was filtered and the filtrate was allowed to stand undisturbed at room temperature. Red crystals suitable for single-crystal X-ray diffraction were obtained after 3 months. The crystals were filtered, washed with methanol thrice, and dried in air (yield 32% based on bppdca). IR (KBr, $\nu\,cm^{-1}$): 3492(m), 3252(m), 1682(s), 1651(s), 1589(s), 1533(s), 1449(s), 1319(s), 1244(s), 1200(s), 1095(s), 799(m), 694(m).

Table 1. Crystallographic data for **1** and **2**.

	1	**2**
Empirical formula	$C_{72}H_{52}N_{24}Ni_2O_8S_4$	$C_{22}H_{28}CoN_6O_9S$
Formula weight	1627.04	611.49
Temperature (K)	298	298
Crystal system	Tetragonal	Triclinic
Space group	$I\bar{4}2d$	$P\bar{1}$
Unit cell dimensions (Å, °)		
α	21.6215(8)	8.9248(11)
b	21.6215(8)	11.5507(14)
c	46.266(3)	13.9825(17)
α	90	105.855(2)
β	90	104.196(2)
γ	90	96.307(2)
Volume (Å^{-3}), Z	21629(2), 8	1319.8(3), 2
Calculated density (g cm^{-3})	0.999	1.539
Goodness-of-fit on F^2	1.021	1.028
Final R indices [$I > 2\sigma(I)$]	0.0647	0.0422
Largest difference peak and hole (e Å^{-3})	0.1692	0.0864

2.3. *Single-crystal structure determination and magnetic susceptibility measurements*

Data collection was performed at 293 K on a Mercury CCD diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods and all calculations were performed using the SHELXL package [7]. All non-hydrogen atoms were refined anisotropically. In **1**, to remove the high residual peaks, the SQUEEZE routine in PLATON was used and structures were then refined again using the data generated. The carbon and sulfur of thiocyanate inside the cage are both disordered over two sites and refined anisotropically. The crystal data for **1** and **2** are summarized in table 1 and selected bond lengths and angles of **1** and **2** are listed in tables 2 and 3, respectively. For **2**, the polycrystalline magnetic susceptibility data were collected on a Quantum Design MPMS (SQUID)-XL magnetometer at temperatures ranging from 2 to 300 K.

3. Results and discussion

3.1. *Syntheses and IR spectra*

The tetragonal molecular cage (**1**) and polymeric macrocyclic (**2**) were synthesized under similar conditions. SO_4^{2-} and SCN^- are present in the solution in the syntheses of **1** and **2**, respectively. However, upon crystallization different anions are incorporated in **1** and **2**. Under the condition, the anion effect for Ni^{2+} and Co^{2+} is identical. Therefore, the different structures in **1** and **2** originate from coordinating preferences of the metal centers. In the absence of SCN^-, the reaction of bppdca with $NiSO_4$ does not give a tetragonal molecular cage-like complex (**1**). However, in the absence of SCN^-, the reaction of bppdca with $CoSO_4$ results in a polymeric macrocyclic complex (**2**). Therefore, we observe the synthesis of **2** in the presence of SCN^-. We consider that the coordinating preference of the metal center is dominant in the assembly of **1** and **2**.

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Ni1–N12	2.044(4)	Ni1–N5^{i}	2.118(4)
Ni1–N1	2.091(4)	Ni1–N9	2.126(4)
Ni1–N6	2.106(4)	Ni1–N13	2.148(3)
N12–Ni1–N1	91.33(17)	N6–Ni1–N9	178.25(14)
N12–Ni1–N6	90.95(16)	N5^{i}–Ni1–N9	89.44(16)
N1–Ni1–N6	91.31(15)	N12–Ni1–N13	179.50(18)
N12–Ni1–N5^{i}	89.87(16)	N1–Ni1–N13	88.73(14)
N1–Ni1–N5^{i}	177.62(17)	N6–Ni1–N13	89.54(13)
N6–Ni1–N5^{i}	90.71(16)	N5^{i}–Ni1–N13	90.05(14)
N12–Ni1–N9	90.79(16)	N9–Ni1–N13	88.72(14)
N1–Ni1–N9	88.50(16)	N12–Ni1–N1	91.33(17)

Symmetry code: ^{i} x, $1/2-y$, $1/4-z$.

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Co1–O8^{i}	2.032(2)	Co1–O4	2.142(2)
Co1–O5	2.0849(19)	Co1–N5^{ii}	2.151(2)
Co1–O3	2.118(2)	Co1–N1	2.164(2)
O8^{i}–Co1–O5	O8^{i}–Co1–O5	O3–Co1–N5^{ii}	O3–Co1–N5^{ii}
O8^{i}–Co1–O3	O8^{i}–Co1–O3	O4–Co1–N5^{ii}	O4—Co1–N5^{ii}
O5–Co1–O3	O5–Co1–O3	O8^{i}–Co1–N1	O8^{i}–Co1–N1
O8^{i}–Co1–O4	O8^{i}–Co1–O4	O5–Co1–N1	O5–Co1–N1
O5–Co1–O4	O5–Co1–O4	O3–Co1–N1	O3–Co1–N1
O3–Co1–O4	O3–Co1–O4	O4–Co1–N1	O4–Co1–N1
O8^{i}–Co1–N5^{ii}	O8^{i}–Co1–N5^{ii}	N5^{ii}–Co1–N1	N5^{ii}–Co1–N1
O5–Co1–N5^{ii}	O5–Co1–N5^{ii}		

Symmetry codes: ^{i} $1-x$, $1-y$, $-z$; ^{ii} x, $1+y$, z.

Indeed, for **1,** SCN^- also have an influence on the formation of tetragonal molecular cage. In the IR spectra, a strong band emerging around 2084 cm^{-1} for **1** and 1095 cm^{-1} for **2** indicate the existence of SCN^- and SO_4^{2-} in **1** and **2**, respectively. The results of the IR spectra of **1** and **2** are consistent with the single-crystal X-ray diffraction analyses.

3.2. *Crystal structures of 1 and 2*

Single-crystal X-ray diffraction analysis confirms that **1** crystallizes in a non-centrosymmetrical space group $I\bar{4}2d$ and features a tetragonal molecular cage. As shown in figure 1, the cage consists of two Ni(II), four clip-like bppdca ligands, and four thiocyanates. Each Ni(II) in a slightly distorted octahedral coordination environment is completed by four nitrogen atoms from four bppdca to construct the equatorial plane and two nitrogen atoms from two thiocyanates occupying the axial sites (figure 1). The Ni–N distances are 2.050(6)–2.165(4) Å and the N–Ni–N angles are 88.6(2)–91.5(2)° and 177.6(2)–179.3(3)°, which are all in agreement with the reported values [8]. Of the four thiocyanates, two are outside the tetragonal cage and the other two are inside the cage.

In comparison with the reported dimeric tetragonal prisms [5], the tetragonal prism in **1** displays lower symmetry. In the cage, only a two-fold axis passes through the vector

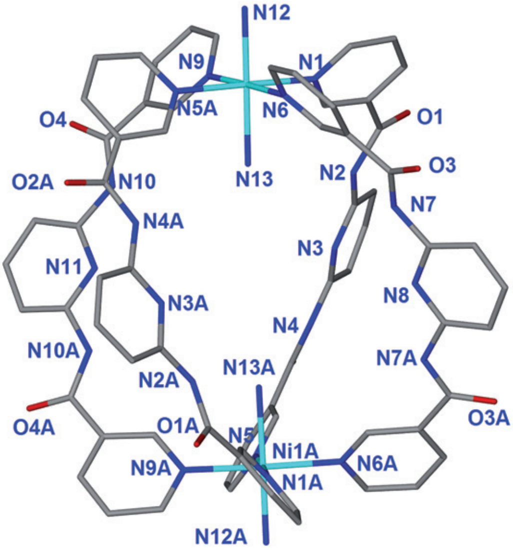

Figure 1. View of the coordination environment of Ni(II) with hydrogen atoms as well as carbon and sulfur of the thiocyanates omitted for clarity. Symmetry code: A, x, $1/2-y$, $1/4-z$.

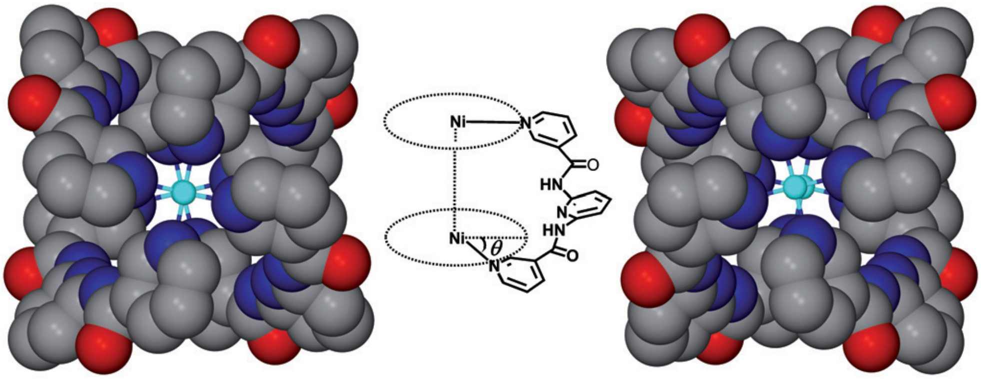

Figure 2. The two types of chiral helicates in **1**: (P, P)-twisted helicates (left) and (M, M)-twisted helicates (right). The middle insert shows the definition of the azimuthal angle θ.

of C26–N11–N8–C35. However, four bppdca ligands are arranged in such a way that pseudo C_{4h} symmetry could be imagined to impose on the tetragonal prisms. The deviation from a highly-symmetric tetragonal prism is probably due to symmetry lowering of bppdca. In **1**, the bppdca ligands are severely twisted and display a non-planar conformation due to free rotation of N_{amide}–$O_{pyridyl}$ bonds. The dihedral angles involving terminal pyridyl rings and the central pyridyl ring are 23.15–49.20°. In each cage four twisted bppdca ligands are screwed in the same direction, which endow the cage with chirality. As seen in figure 2, the azimuthal angles θ relating the two $\{NiN_4\}$ units are 64.93, 65.68, and 63.87°, respectively. The pitch of the helicate can be

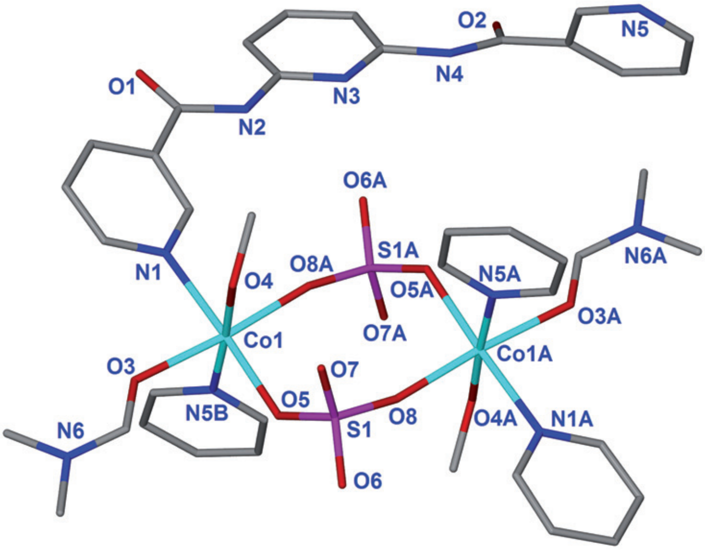

Figure 3. The coordination environments of the dinuclear Co(II) ions with hydrogen atoms omitted for clarity. Symmetry codes: A, $1-x$, $1-y$, $-z$; B, x, $1+y$, z.

estimated by the Ni···Ni separation of 10.386(8) Å. However, since the screw directions of adjacent cages are contrary, we obtain two types of chiral isomers, (*P*, *P*)-twisted helicates and (*M*, *M*)-twisted helicates (figure 2). Upon stacking, the layers, which are constructed by the homo-chiral (*P*, *P*)-twisted helicates or (*M*, *M*)-twisted helicates, pack themselves alternately and form an ABAB arrangement. On the whole, **1** is a mesomer and shows no chirality.

Similar quadruple-stranded helicates remain rare. The first example is confirmed by electrospray mass spectrometry as a double-charged anion, which was constructed by two Eu(III) cations and four bis-diketone ligands [9a]. However, there was no structural evidence. The first fully structurally characterized quadruple-stranded helicates were reported by Raymond in 2006, which were Th(III)-bis-diketone complexes [9b]. Recently two examples of planar four-coordinate Pd(II) quadruple-stranded helicates were also characterized [9c, 9d]. However, the quadruple-stranded helicates based on 3d metal ions are not yet reported.

In **2**, two bppdca ligands, four Co(II) ions, and four SO_4^{2-} ions form a 36-membered ring. Each Co(II) is six-coordinate N_2O_4 octahedral (figures 3 and 4). Two oxygen atoms from two SO_4^{2-}, one oxygen atom from DMF, and a nitrogen atom from a pyridyl group of bppdca form the equatorial plane. One oxygen atom from one methanol and one nitrogen atom of bppdca complete the coordination sphere of cobalt(II) at the axial sites. The Co–N bond lengths are 2.151(2) and 2.164(2) Å, and Co–O bond lengths are 2.032(2)–2.142(2) Å, which are comparable with the reported values [10]. The two centrosymmetric cobalt(II) ions are bridged by two bidentate-bridging SO_4^{2-}, which can be abstracted to a 4-connected node. By the coordination of ditopic bppdca to cobalt(II), a polymeric chain based on metalated macrocycles is formed. Two free methanols are trapped inside the 36-member macrocycle through hydrogen bonding with an oxygen atom of SO_4^{2-}, with an O···O distance of 2.795 Å.

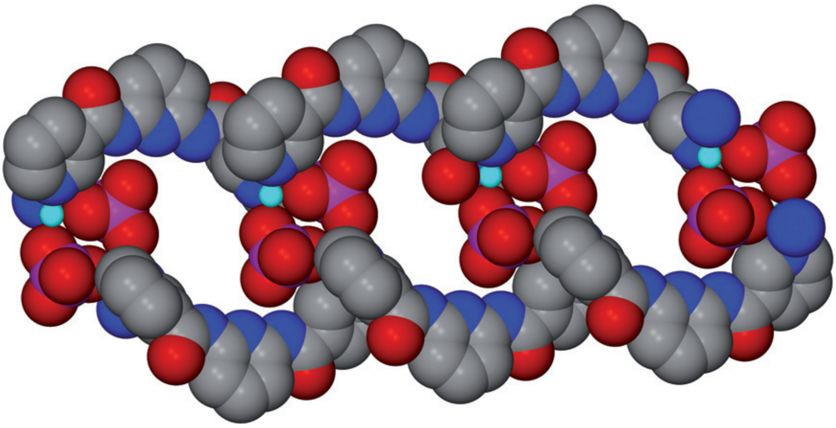

Figure 4. View of the polymeric macrocycle chain linked by the 4-connected node $Co_2(SO_4)_2$ with a coordinating methanol and DMF omitted for clarity.

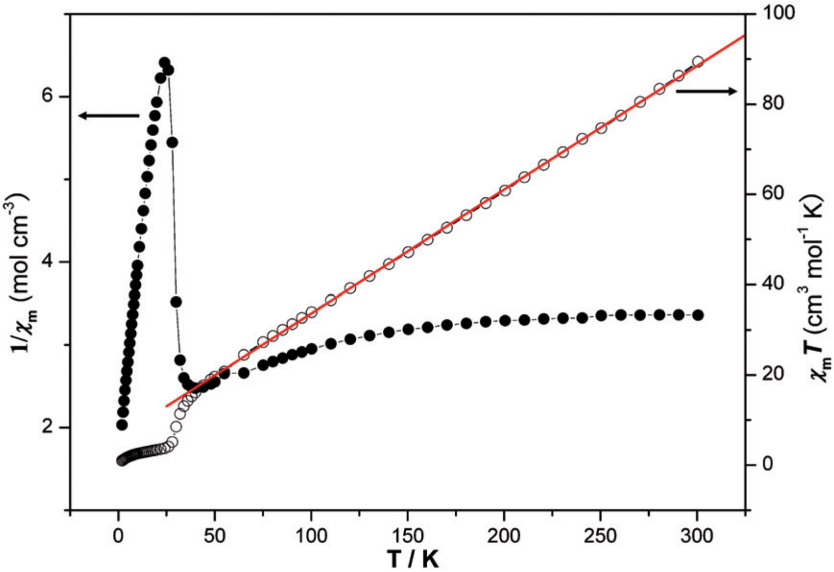

Figure 5. Temperature dependence of the magnetic susceptibility curves for **2**. The solid line shows the Curie–Weiss fitting.

3.3. *Magnetism of 2*

The magnetic susceptibility was measured on a polycrystalline sample of **2** under an applied field of 1000 Oe, as shown in figure 5. The $\chi_M T$ value at 300 K is 3.36 $cm^3 mol^{-1} K$ (5.18μ_B) per Co(II) ion, which is much higher than the expected value (1.88 $cm^3 mol^{-1} K$, 3.87μ_B) for a magnetically isolated spin-only Co(II) ion with $S = 3/2$ and $g = 2.00$ but close to the value expected when the spin momentum and orbital momentum exist independently [$5.20\mu_B$; $\mu_{LS} = [L(L+1) + 4\ S(S+1)]^{1/2}$; $L = 3$, $S = 3/2$] [11]. This clearly indicates the presence of significant orbital angular contributions, common for high-spin Co(II) in an octahedral coordination environment. Along with the temperature decreasing from 300 K, the magnetic moments decrease gradually and reach a minimum of $2.48\,\mathrm{cm^3\,mol^{-1}\,K}$ at 40 K, due to depopulation of the Stark sublevels of octahedral Co(II), which display a strong spin–orbit coupling [12]. The reciprocal molar magnetic susceptibility data obey the Curie–Weiss law in the high temperature region of 50–300 K with a Curie constant of $C = 3.65\,\mathrm{cm^3\,mol^{-1}\,K}$ and a Weiss constant of $\theta = -22.67\,\mathrm{K}$. The negative value of the Weiss temperature indicates that the dominant interactions between Co(II) ions are antiferromagnetic. As the temperature is lowered, $\chi_M T$ increases abruptly to a maximum of $6.41\,\mathrm{m^3\,mol^{-1}\,K}$ at 24 K, and then drops quickly and goes down to a minimum of $2.03\,\mathrm{m^3\,mol^{-1}\,K}$ at 2 K. This deviation below 40 K is mainly the result of the presence of intramolecular weak ferromagnetism caused by small uncompensated AF spin-canting or some impurity [13].

4. Conclusions

Reactions of a clip-like bis-pyridyl-bis-amide ligand with nickel(II) and cobalt(II) salts, we synthesized a tetragonal molecular cage **1** and a polymeric metalated macrocycle **2**. A comparison between the structures of **1** and **2** suggests that the coordination configurations of the metal ions play an important role in the process of self-assembly. In **1**, if we omit the two terminal thiocyanates sitting at the axial sites and the nickel(II) ion is square-planar. Therefore, four bppdca ligands clamp two nickel(II) ions to form a tetragonal prism. Notably, as four severely twisted bppdca ligands in each cage are screwed in the same direction in **1**, each cage is deemed as a rare homochiral quadruple-stranded helicate. In **2**, the 4-connected node $Co_2(SO_4)_2$ subunit has a severe deviation from planar (the N–centroid$_{(Co\cdots Co)}$–N angles are 45.58 and 134.42°). Accordingly, two bppdca connect two $Co_2(SO_4)_2$ subunits into a macrocycle and further expand into a polymeric chain. Perhaps, this work will enhance rational design and synthesis of metalated macrocyclic and cage-like molecules. Further research is under way and systematic results will be reported later.

Acknowledgments

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